Theor Chem Acc (1997) 96:248–255

Theoretical
Chemistry Accounts

Atomic ionization potentials and electron affinities with relativistic and mass corrections

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Received: 28 January 1997 / Accepted: 4 March 1997

Abstract. Relativistic corrections to ionization potentials (IPs) and electron affinities (EAs) of atoms with an atomic number $Z \leq 54$ are examined based on the first-order perturbation theory with an approximate Schrödinger form of the Dirac-Coulomb-Breit Hamiltonian. Using a Hartree-Fock (HF) wave function from the numerical HF method as the unperturbed function, both the *LS*-non-splitting and fine-structure corrections are evaluated together with the normal and specific mass corrections. The *LS*-non-splitting corrections are found to be important for IPs and EAs of transition metal atoms. The fine-structure corrections are generally larger in magnitude than the *LS*-non-splitting corrections for the atoms of groups 13–18 with $Z \geq 31$, and can never be neglected. Comparison of the IPs and EAs presented here and experimental IPs and EAs gives an estimation of the electron correlation correction for these properties. For some light atoms, the estimated values agree with the results directly obtained from correlated calculations.

Key words: Relativistic correction – Mass correction – Ionization potential – Electron affinity – Atoms

1 Introduction

The total energy E of an atom may be expressed (see, e.g. [1]) as the sum of four contributions:

$$E = E_{\mathrm{HF}} + E_{\mathrm{mass}} + E_{\mathrm{rel}} + E_{\mathrm{corr}} \qquad (1)$$

where E_{HF} is the non-relativistic Hartree-Fock (HF) energy, E_{mass} the mass corrections, E_{rel} the relativistic corrections and E_{corr} the electron correlation corrections. The HF limit energies have been reported in literature [1–4] based on the numerical HF method [3, 5]. Results with an improved accuracy have also been reported for neutral atoms not only in the ground state [6, 7] but also in low-lying excited states [8–10] as well as singly charged cations and anions [11, 12]. The mass correction energies, one arising from the change in reduced mass between one atom and another and the other arising from the separation of the centre-of-mass motion from the internal motion, have not usually been considered. Systematic studies on the relativistic corrections for atoms are found in [1] and [13]. For a complete bibliography on relativistic methods and calculations published between 1916 and 1992, including various reviews, see Refs. [14, 15]. The electron correlation energy can be derived from correlated calculations, though accurate results are available only for some few-electron atoms for which the interelectronic variable r_{ij} can be explicitly incorporated into wave functions.

Since Eq. (1) holds both for neutral and charged atoms, a similar decomposition is possible for ionization potentials (IPs) and electron affinities (EAs), which are fundamental properties of atoms subject to direct experimental measurement (see, e.g. [16, 17]). Recently, we reported the HF contributions to IPs and EAs for atoms with atomic number $Z \leq 54$ based on accurate non-relativistic numerical HF calculations [11]. For IPs, the HF values showed a good parallelism with the experimental results. The differences ranged from 0.05 to 2.1 eV, and were generally larger for the transition metal atoms. The HF and experimental EAs also showed parallel behaviour, but the parallelism was poorer than that of IPs particularly for the transition metal atoms. In some cases, the HF EAs were found to be negative. The relativistic and correlation corrections to IPs of 2- to 18-electron atomic ions were examined [18, 19]. For IPs and excitation energies of transition atoms, the significance of relativistic corrections was reported [20] based on the Cowan-Griffin approximation [21], which considers only the mass-velocity and Darwin corrections. The relativistic corrections to EAs were discussed [22] for alkali and halogen atoms. Very recently [23], one of us studied relativistic corrections to EAs systematically and found that they give non-trivial contributions. However, the relativistic correction examined [23] was only the *LS*-non-splitting contribution, and the fine-structure contribution was not included.

In the present paper, we systematically report relativistic corrections to IPs and EAs of atoms with $Z \leq 54$,

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treating an approximate Schrödinger form of the Dirac-Coulomb-Breit Hamiltonian as a perturbation. Numerical HF wave functions with improved accuracy are used as the unperturbed wave function, and both the *LS*-non-splitting and fine-structure corrections are studied. The mass corrections are also examined. In the next section, we outline the theoretical ground and computational method. The results are presented and discussed in Sect. 3. Except for the IPs of light atoms, the mass corrections are small. Both for IPs and EAs, we find that the *LS*-non-splitting correction is more important than the fine-structure correction for transition metal atoms. However, the opposite is true for atoms of groups 13–18 with $Z \geq 31$. All energies throughout this paper are given in eV where 1 hartree = 27.2113961 eV [24].

2 Theoretical ground and computational method

The mass correction E_{mass} in Eq. (1) consists of two contributions:

$$E_{\mathrm{mass}} = E_{\mathrm{nm}} + E_{\mathrm{sm}} \ , \tag{2}$$

where E_{nm} denotes the normal mass correction, which takes into account the fact that the electron-reduced mass is different from one atom to another. The E_{sm} means specific mass (or mass polarization) correction, which arises from the separation of the centre-of-mass motion and internal motion. These mass corrections are not relativistic effects, but they are not considered in usual non-relativistic calculations.

By expanding the Dirac-Coulomb-Breit relativistic Hamiltonian with respect to $1/c$ and retaining the terms correct to the order $1/c^2$ for electron-electron interactions and the terms correct to the order $1/(Mc^2)$ for electron-nucleus interactions, we obtain (see, e.g. [25–28]) an approximate relativistic Hamiltonian for atoms in the non-relativistic Schrödinger form, where c and M stand for the speed of light and nuclear mass, respectively. We can then evaluate the relativistic corrections through the first-order perturbation theory by using a non-relativistic wave function as the unperturbed wave function. The relativistic corrections thus obtained are partitioned into two groups:

$$E_{\mathrm{rel}} = E_{\mathrm{LS}} + E_{\mathrm{FS}} \ . \tag{3}$$

The first term E_{LS} is the so-called *LS*-non-splitting correction, and depends on the orbital L and spin S angular momentum quantum numbers of the level of the atom under consideration. The E_{LS} consists of five contributions with different physical meanings:

$$E_{\mathrm{LS}} = E_{\mathrm{mv}} + E_{\mathrm{D1}} + E_{\mathrm{D2}} + E_{\mathrm{ssc}} + E_{\mathrm{oo}} \ , \tag{4}$$

where E_{mv} represents the mass-velocity term, E_{D1} the one-electron Darwin term, E_{D2} the two-electron Darwin term, E_{ssc} the spin-spin contact term and E_{oo} the orbit-orbit interaction term. The second term E_{FS} in Eq. (3) is the fine-structure correction and depends not only on L and S but also on the total angular momentum quantum number J. It contains two contributions:

$$E_{\mathrm{FS}} = E_{\mathrm{so}} + E_{\mathrm{ssd}} \ , \tag{5}$$

where E_{so} and E_{ssd} represent the spin-orbit and spin-spin-dipole interaction terms, respectively. In order to obtain E_{FS}, the Hamiltonian matrix of the above two interactions is diagonalized, where the matrix elements are evaluated with the configuration state functions with different orbital L and spin S angular momenta obtained from the same configurational space as the unperturbed HF wave function. For the explicit forms of the operators of individual corrections appearing on the right-hand sides of Eqs. (2), (4) and (5), see for example, [1, 25–31] except that E_{nm} is approximated by $-(m/M)E_{\mathrm{HF}}$ in the present context where m and M are electron and nuclear masses, respectively. Also included implicitly in the above relativistic corrections is the relativistic mass correction [33, 34] which takes into account the difference of the electron and reduced masses appearing in the relativistic Hamiltonian.

We have first generated non-relativistic HF wave functions numerically using an enhanced version of the computer program MCHF72 [35]. An improved accuracy has been achieved by increasing the number of radial mesh points and reducing the interval between the meshes, based on a careful examination of the numerical procedures involved in MCHF72. All our numerical HF orbitals are convergent to 1×10^{-10} at any radial point, and the HF total energies are reliable in ten significant figures. Table 1 lists the ground levels of the neutral atoms and singly charged ions examined. It should be noted that for the sake of convenience, the electronic configuration of an ion is given in the table as the change from its parent neutral species. For the Sc$^-$ and Pd$^-$ anions, we could not obtain a convergent HF solution for the experimental ground state [17], and we excluded them from the present study of EAs.

The first-order perturbation evaluation of the above-mentioned relativistic corrections was carried out using the RIAS program [36], which we modified to match our improved numerical HF wave functions. In addition to the electronic information summarized in Table 1, the relativistic corrections require the nuclear mass to be specified. For each atom (or ion), we have employed the atomic mass of the most naturally abundant or long-lived isotope given in [24]. All the other required physical constants such as c and m were also taken from [24].

To check the accuracy of the present perturbative calculations, we have subtracted for rare-gas atoms the Breit corrections and compared the relativistic corrections with the numerical Dirac-HF results of Desclaux [13]. For Ar ($Z = 18$), Kr ($Z = 36$), and Xe ($Z = 54$) atoms, the present values were found to be 99, 97 and 93%, respectively, of the non-perturbative values, though the latter results [13] were obtained from a finite-size nucleus model.

3 Results and discussion

3.1 Ionization potentials (IPs)

According to Eq. (3), the relativistic correction IP_{rel} to IP, owing to the approximate Dirac-Coulomb-Breit-

Table 1. Experimental ground levels of the neutrals, cations, and anions examined in this study

Z^a	Atom	Neutral	Cation	Anion
1	H	1*s* (1), $^2S_{1/2}$		+1*s* (1), $^1S_0$
2	He	1*s* (2), $^1S_0$	−1*s*(1), $^2S_{1/2}$	
3	Li	[He] 2*s*(1), $^2S_{1/2}$	−2*s*(1), $^1S_0$	+2*s* (1), $^1S_0$
4	Be	[He] 2*s*(2), $^1S_0$	−2*s*(1), $^2S_{1/2}$	
5	B	[He] 2*s*(2) 2*p*(1), $^2P_{1/2}$	−2*p*(1), $^1S_0$	+2*p*(1), $^3P_0$
6	C	[He] 2*s*(2) 2*p*(2), $^3P_0$	−2*p*(1), $^2P_{1/2}$	+2*p*(1), $^4S_{3/2}$
7	N	[He] 2*s*(2) 2*p*(3), $^4S_{3/2}$	−2*p*(1), $^3P_0$	+2*p*(1), $^3P_2$
8	O	[He] 2*s*(2) 2*p*(4), $^3P_2$	−2*p*(1), $^4S_{3/2}$	+2*p*(1), $^2P_{3/2}$
9	F	[He] 2*s*(2) 2*p*(5), $^2P_{3/2}$	−2*p*(1), $^3P_2$	+2*p*(1), $^1S_0$
10	Ne	[He] 2*s*(2) 2*p*(6), $^1S_0$	−2*p*(1), $^2P_{3/2}$	
11	Na	[Ne] 3*s*(1), $^2S_{1/2}$	−3*s*(1), $^1S_0$	+3*s*(1), $^1S_0$
12	Mg	[Ne] 3*s*(2), $^1S_0$	−3*s*(1), $^2S_{1/2}$	
13	Al	[Ne] 3*s*(2) 3*p*(1), $^2P_{1/2}$	−3*p*(1), $^1S_0$	+3*p*(1), $^3P_0$
14	Si	[Ne] 3*s*(2) 3*p*(2), $^3P_0$	−3*p*(1), $^2P_{1/2}$	+3*p*(1), $^4S_{3/2}$
15	P	[Ne] 3*s*(2) 3*p*(3), $^4S_{3/2}$	−3*p*(1), $^3P_0$	+3*p*(1), $^3P_2$
16	S	[Ne] 3*s*(2) 3*p*(4), $^3P_2$	−3*p*(1), $^4S_{3/2}$	+3*p*(1), $^2P_{3/2}$
17	Cl	[Ne] 3*s*(2) 3*p*(5), $^2P_{3/2}$	−3*p*(1), $^3P_2$	+3*p*(1), $^1S_0$
18	Ar	[Ne] 3*s*(2) 3*p*(6), $^1S_0$	−3*p*(1), $^2P_{3/2}$	
19	K	[Ar] 4*s*(1), $^2S_{1/2}$	−4*s*(1), $^1S_0$	+4*s*(1), $^1S_0$
20	Ca	[Ar] 4*s*(2), $^1S_0$	−4*s*(1), $^2S_{1/2}$	
21	Sc	[Ar] 4*s*(2) 3*d*(1), $^2D_{3/2}$	−4*s*(1), $^3D_1$	+4*p*(1), $^1D_2$
22	Ti	[Ar] 4*s*(2) 3*d*(2), $^3F_2$	−4*s*(1), $^4F_{3/2}$	+3*d*(1), $^4F_{3/2}$
23	V	[Ar] 4*s*(2) 3*d*(3), $^4F_{3/2}$	−4*s*(2) + 3*d*(1), $^5D_0$	+3*d*(1), $^5D_0$
24	Cr	[Ar] 4*s*(1) 3*d*(5), $^7S_3$	−4*s*(1), $^6S_{5/2}$	+4*s*(1), $^6S_{5/2}$
25	Mn	[Ar] 4*s*(2) 3*d*(5), $^6S_{5/2}$	−4*s*(1), $^7S_3$	+3*d*(1), $^5D_4$
26	Fe	[Ar] 4*s*(2) 3*d*(6), $^5D_4$	−4*s*(1), $^6D_{9/2}$	+3*d*(1), $^4F_{9/2}$
27	Co	[Ar] 4*s*(2) 3*d*(7), $^4F_{9/2}$	−4*s*(2) + 3*d*(1), $^3F_4$	+3*d*(1), $^3F_4$
28	Ni	[Ar] 4*s*(2) 3*d*(8), $^3F_4$	−4*s*(2) + 3*d*(1), $^2D_{5/2}$	+3*d*(1), $^2D_{5/2}$
29	Cu	[Ar] 4*s*(1) 3*d*(10), $^2S_{1/2}$	−4*s*(1), $^1S_0$	+4*s*(1), $^1S_0$
30	Zn	[Ar] 4*s*(2) 3*d*(10), $^1S_0$	−4*s*(1), $^2S_{1/2}$	
31	Ga	[Ar] 4*s*(2) 3*d*(10) 4*p*(1), $^2P_{1/2}$	−4*p*(1), $^1S_0$	+4*p*(1), $^3P_0$
32	Ge	[Ar] 4*s*(2) 3*d*(10) 4*p*(2), $^3P_0$	−4*p*(1), $^2P_{1/2}$	+4*p*(1), $^4S_{3/2}$
33	As	[Ar] 4*s*(2) 3*d*(10) 4*p*(3), $^4S_{3/2}$	−4*p*(1), $^3P_0$	+4*p*(1), $^3P_2$
34	Se	[Ar] 4*s*(2) 3*d*(10) 4*p*(4), $^3P_2$	−4*p*(1), $^4S_{3/2}$	+4*p*(1), $^2P_{3/2}$
35	Br	[Ar] 4*s*(2) 3*d*(10) 4*p*(5), $^2P_{3/2}$	−4*p*(1), $^3P_2$	+4*p*(1), $^1S_0$
36	Kr	[Ar] 4*s*(2) 3*d*(10) 4*p*(6), $^1S_0$	−4*p*(1), $^2P_{3/2}$	
37	Rb	[Kr] 5*s*(1), $^2S_{1/2}$	−5*s*(1), $^1S_0$	+5*s*(1), $^1S_0$
38	Sr	[Kr] 5*s*(2), $^1S_0$	−5*s*(1), $^2S_{1/2}$	
39	Y	[Kr] 5*s*(2) 4*d*(1), $^2D_{3/2}$	−4*d*(1), $^1S_0$	+5*p*(1), $^1D_2$
40	Zr	[Kr] 5*s*(2) 4*d*(2), $^3F_2$	−5*s*(1), $^4F_{3/2}$	+4*d*(1), $^4F_{3/2}$
41	Nb	[Kr] 5*s*(1) 4*d*(4), $^6D_{1/2}$	−5*s*(1) $^5D_0$	+5*s*(1), $^5D_0$
42	Mo	[Kr] 5*s*(1) 4*d*(5), $^7S_3$	−5*s*(1), $^6S_{5/2}$	+5*s*(1), $^6S_{5/2}$
43	Tc	[Kr] 5*s*(2) 4*d*(5), $^6S_{5/2}$	−5*s*(1), $^7S_3$	+4*d*(1), $^5D_4$
44	Ru	[Kr] 5*s*(1) 4*d*(7), $^5F_5$	−5*s*(1), $^4F_{9/2}$	+5*s*(1), $^4F_{9/2}$
45	Rh	[Kr] 5*s*(1) 4*d*(8), $^4F_{9/2}$	−5*s*(1) $^3F_4$	+5*s*(1), $^3F_4$
46	Pd	[Kr] 5*s*(0) 4*d*(10), $^1S_0$	−4*d*(1) $^2D_{5/2}$	+5*s*(1), $^2S_{1/2}$
47	Ag	[Kr] 5*s*(1) 4*d*(10), $^2S_{1/2}$	−5*s*(1), $^1S_0$	+5*s*(1), $^1S_0$
48	Cd	[Kr] 5*s*(2) 4*d*(10), $^1S_0$	−5*s*(1), $^2S_{1/2}$	
49	In	[Kr] 5*s*(2) 4*d*(10) 5*p*(1), $^2P_{1/2}$	−5*p*(1), $^1S_0$	+5*p*(1), $^3P_0$
50	Sn	[Kr] 5*s*(2) 4*d*(10) 5*p*(2), $^3P_0$	−5*p*(1), $^2P_{1/2}$	+5*p*(1), $^4S_{3/2}$
51	Sb	[Kr] 5*s*(2) 4*d*(10) 5*p*(3), $^4S_{3/2}$	−5*p*(1), $^3P_0$	+5*p*(1), $^3P_2$
52	Te	[Kr] 5*s*(2) 4*d*(10) 5*p*(4), $^3P_2$	−5*p*(1), $^4S_{3/2}$	+5*p*(1), $^2P_{3/2}$
53	I	[Kr] 5*s*(2) 4*d*(10) 5*p*(5), $^2P_{3/2}$	−5*p*(1), $^3P_2$	+5*p*(1), $^1S_0$
54	Xe	[Kr] 5*s*(2) 4*d*(10) 5*p*(6), $^1S_0$	−5*p*(1), $^2P_{3/2}$	

[a] Z = atomic number

Pauli Hamiltonian within the HF approximation, is given by

$$IP_{\mathrm{rel}} = IP_{\mathrm{LS}} + IP_{\mathrm{FS}} \quad . \tag{6}$$

where

$$IP_{\mathrm{LS}} = E_{\mathrm{LS}}(\mathrm{cation}) - E_{\mathrm{LS}}(\mathrm{neutral}) \quad , \tag{7}$$

$$IP_{\mathrm{FS}} = E_{\mathrm{FS}}(\mathrm{cation}) - E_{\mathrm{FS}}(\mathrm{neutral}) \tag{8}$$

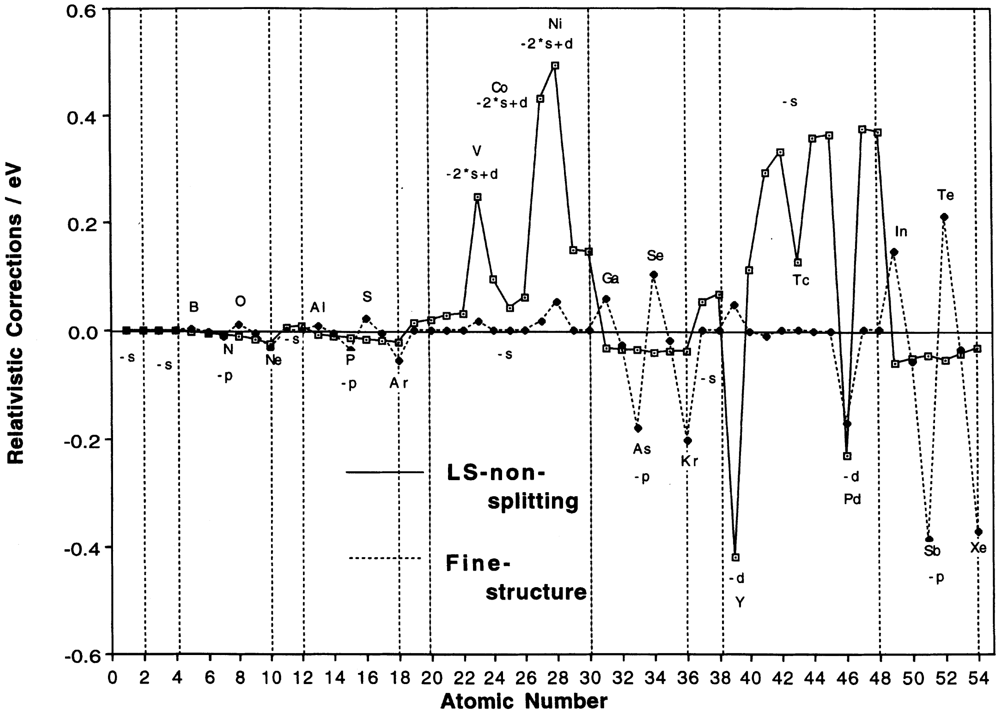
in which E_{LS} is negative and E_{FS} is zero or negative. For the 54 atoms examined, Table 2 presents the nonrelativistic HF IP, the relativistic correction IP_{rel} and its components (IP_{LS} and IP_{FS}) and the relativistic HF IP. Also given in Table 2 are the mass corrections, but their contribution was found to be small except for very light atoms. In Fig. 1, we plot IP_{LS} and IP_{FS} as a function of the atomic number Z. Figure 1 and Table 2 clearly show that the relative significance of the two relativistic corrections IP_{LS} and IP_{FS} is very different depending on the ionization process. The *LS*-non-splitting correction is dominant when an *s* or *d* electron is ionized, while the fine-structure correction is dominant when a *p* electron is ionized.

Table 2. Comparison of the non-relativistic Hartree-Fock (HF), relativistic HF, and experimental IPs (in eV)

Atom		Non-relativistic HF IP	Mass correction		Relativistic correction			Relativistic HF IP	Experimental IP
			Normal	Specific	LS-non-splitting	Fine-structure	Sum		
1	H	13.60570	−0.00741	0.00000	0.00018	0.00000	0.00018	13.59847	13.59844
2	He	23.44752	−0.00321	0.00000	−0.00101	0.00000	−0.00101	23.44330	24.58741
3	Li	5.34192	−0.00042	0.00000	0.00031	0.00000	0.00031	5.34181	5.39172
4	Be	8.04446	−0.00049	0.00000	0.00098	0.00000	0.00098	8.04495	9.32263
5	B	7.93173	−0.00040	0.00055	−0.00286	0.00177	−0.00109	7.93079	8.29803
6	C	10.78647	−0.00049	0.00064	−0.00514	−0.00242	−0.00756	10.77905	11.26030
7	N	13.95752	−0.00055	0.00067	−0.00851	−0.01263	−0.02114	13.93650	14.53414
8	O	11.88574	−0.00041	0.00059	−0.01132	0.01208	0.00077	11.88669	13.61806
9	F	15.71810	−0.00045	0.00060	−0.01686	−0.00653	−0.02339	15.69486	17.42282
10	Ne	19.84484	−0.00055	0.00068	−0.02419	−0.03487	−0.05906	19.78591	21.56454
11	Na	4.95109	−0.00012	0.00001	0.00604	0.00000	0.00604	4.95701	5.13908
12	Mg	6.60765	−0.00015	0.00001	0.00948	0.00000	0.00948	6.61699	7.64624
13	Al	5.49770	−0.00011	0.00011	−0.00964	0.00818	−0.00146	5.49624	5.98577
14	Si	7.65270	−0.00015	0.00014	−0.01225	−0.00508	−0.01732	7.63537	8.15169
15	P	10.04114	−0.00018	0.00016	−0.01516	−0.03605	−0.05121	9.98992	10.48669
16	S	9.02638	−0.00016	0.00017	−0.01726	0.02373	0.00647	9.03286	10.36001
17	Cl	11.79564	−0.00019	0.00019	−0.02043	−0.00595	−0.02638	11.76926	12.96764
18	Ar	14.77520	−0.00020	0.00019	−0.02384	−0.05721	−0.08105	14.69415	15.75962
19	K	4.00572	−0.00006	0.00002	0.01435	0.00000	0.01435	4.02003	4.34066
20	Ca	5.12046	−0.00007	0.00002	0.01948	0.00000	0.01948	5.13989	6.11316
21	Sc	5.34905	−0.00007	0.00002	0.02686	−0.00034	0.02652	5.37552	6.56144
22	Ti	5.51293	−0.00006	0.00001	0.03134	−0.00024	0.03110	5.54398	6.8282
23	V	5.81110	−0.00006	−0.00029	0.24920	0.01593	0.26512	6.07587	6.7463
24	Cr	5.90441	−0.00008	−0.00003	0.09709	0.00000	0.09709	6.00139	6.76664
25	Mn	5.90131	−0.00005	0.00000	0.04354	0.00000	0.04354	5.94479	7.43402
26	Fe	6.27639	−0.00005	−0.00003	0.06104	−0.00057	0.06046	6.33677	7.9024
27	Co	7.77710	−0.00008	−0.00035	0.43002	0.01627	0.44629	8.22296	7.8810
28	Ni	7.61399	−0.00005	−0.00035	0.49405	0.05412	0.54817	8.16176	7.6398
29	Cu	6.40828	−0.00005	−0.00005	0.14808	0.00000	0.14808	6.55626	7.72638
30	Zn	7.63473	−0.00008	0.00000	0.14710	0.00000	0.14710	7.78175	9.39405
31	Ga	5.47733	−0.00003	0.00003	−0.03475	0.05812	0.02337	5.50070	5.99930
32	Ge	7.43532	−0.00005	0.00005	−0.03532	−0.02759	−0.06291	7.37241	7.900
33	As	9.53267	−0.00005	0.00005	−0.03597	−0.18164	−0.21761	9.31506	9.8152
34	Se	8.40936	−0.00005	0.00005	−0.04169	0.10381	0.06212	8.47148	9.75238
35	Br	10.77903	−0.00008	0.00008	−0.04019	−0.02054	−0.06074	10.71830	11.81381
36	Kr	13.26781	−0.00008	0.00008	−0.03823	−0.20155	−0.23979	13.02803	13.99961
37	Rb	3.74219	−0.00003	0.00003	0.05437	0.00000	0.05437	3.79656	4.17713
38	Sr	4.67788	−0.00003	0.00003	0.06795	0.00000	0.06795	4.74583	5.69484
39	Y	5.74944	−0.00005	0.00011	−0.41955	0.04849	−0.37105	5.37844	6.217
40	Zr	5.05479	−0.00003	0.00000	0.11138	−0.00248	0.10890	5.16366	6.63390
41	Nb	5.66582	−0.00005	−0.00003	0.29220	−0.01102	0.28118	5.94691	6.75885
42	Mo	5.87214	−0.00005	0.00000	0.33345	0.00000	0.33345	6.20553	7.09243
43	Tc	5.28927	−0.00003	0.00000	0.12593	0.00000	0.12593	5.41518	7.28
44	Ru	5.91935	−0.00003	−0.00003	0.35704	−0.00419	0.35285	6.27215	7.36050
45	Rh	5.91935	−0.00003	0.00000	0.36471	−0.00373	0.36099	6.28031	7.45890
46	Pd	6.66935	−0.00003	0.00011	−0.23026	−0.17285	−0.40311	6.26632	8.3369
47	Ag	5.90866	−0.00003	−0.00003	0.37546	0.00000	0.37546	6.28406	7.57624
48	Cd	6.92623	−0.00003	−0.00003	0.36997	0.00000	0.36997	7.29614	8.99367
49	In	5.19095	−0.00003	0.00003	−0.06123	0.14710	0.08588	5.27683	5.78636
50	Sn	6.89461	−0.00003	0.00003	−0.05374	−0.05782	−0.11157	6.78304	7.34381
51	Sb	8.69078	−0.00003	0.00003	−0.04686	−0.38523	−0.43209	8.25869	8.64
52	Te	7.63729	−0.00003	0.00003	−0.05622	0.21032	0.15410	7.79138	9.0096
53	I	9.62258	−0.00005	0.00005	−0.04596	−0.03679	−0.08275	9.53983	10.45126
54	Xe	11.68504	−0.00005	0.00003	−0.03502	−0.37062	−0.40564	11.27937	12.12987

We will discuss first the cases where the *LS*-non-splitting correction is significant. The ionizations in He, group 1 (alkali), 2 (alkali-earth) and 3–12 (transition metal) atoms fall into this category. Although we have not shown the parent relativistic energies of neutrals and cations, the absolute value of the *LS*-non-splitting energy $|E_{\mathrm{LS}}|$ for cations decreases compared with that for neutrals, leading to a positive IP_{LS} and therefore to a positive IP_{rel} in these atoms. The reason why the ionization of the outermost *s* electron decreases $|E_{\mathrm{LS}}|$ is as follows: In the correction E_{LS}, the mass velocity E_{mv} and one-electron Darwin E_{D1} corrections are the main terms. They are large when the electron density around or at the nucleus is large. The removal of the outermost *s*

Fig. 1. *LS*-non-splitting and fine-structure contributions to ionization potentials (IPs) as a function of atomic number *Z*



electron reduces the density distribution in this region resulting in a smaller $|E_{\mathrm{LS}}|$ in cations. We find an abrupt increase of IP_{LS} for V, Co, and Ni atoms. As shown in Table 1, the 4*s* electron ionization in these atoms induces the de-excitation of the remaining 4*s* electron to the 3*d* orbital, which brings a further reduction of $|E_{\mathrm{LS}}|$ for the resultant cations and an increase in IP_{rel}. We also find in Fig. 1 that a sharp decrease in IP_{LS} appears at Y and Pd atoms. This can be explained by the fact that in these two atoms, a 4*d* electron is ionized instead of a 5*s* electron; this introduces the contraction of the electron density in the cations and, in turn, enlarges $|E_{\mathrm{LS}}|$, giving a negative IP_{LS}, and decreasing IP_{rel}.

We next discuss the ionization processes where the fine-structure part is dominant in the relativistic corrections. This is the case for atoms of groups 13–18, B–Ne, Al–Ar, Ga–Kr, and In–Xe. When a *p* electron is ionized in these atoms, $|E_{\mathrm{LS}}|$ slightly increases for the same reason as dicussed for the 4*d* electron ionization in Y and Pd. However, $|IP_{\mathrm{LS}}|$s for the atoms of groups 13–18 are small, since the *p* electron in typical elements is in the outermost subshell, and the removal of this electron causes a small contraction of the inner orbitals in contrast to the case of the 4*d* electron (see the solid line in Fig. 1 for atoms of groups 13–18). Thus the fine-structure correction is the predominant part of the relativistic corrections for atoms of groups 13–18. We see in the figure that the atoms in groups 13 (B, Al, Ga, and In) and 16 (O, S, Se, and Te) have positive IP_{FS}. This is because these cations have zero orbital angular momentum and $E_{\mathrm{FS}}(\mathrm{cation}) = 0$ in Eq. (8). On the other hand, we find a negative contribution of IP_{FS} for the group 15 atoms N, P, As, and Sb. This is also reasonable, since the orbital angular momentum is now zero for the neutrals and $E_{\mathrm{FS}}(\mathrm{neutral}) = 0$ in Eq. (8).

3.2 Electron affinities (EAs)

Similar to IP_{rel}, the relativistic correction EA_{rel} to the EA is expressed as

$$EA_{\mathrm{rel}} = EA_{\mathrm{LS}} + EA_{\mathrm{FS}} \tag{9}$$

where

$$EA_{\mathrm{LS}} = E_{\mathrm{LS}}(\mathrm{neutral}) - E_{\mathrm{LS}}(\mathrm{anion}) \ , \tag{10}$$

$$EA_{\mathrm{FS}} = E_{\mathrm{FS}}(\mathrm{neutral}) - E_{\mathrm{FS}}(\mathrm{anion}) \ . \tag{11}$$

Table 3 summarizes these quantities for the 41 atoms examined as well as the HF contribution and the mass correction. The last correction is negligibly small for EAs. In Fig. 2, EA_{LS} and EA_{FS} are also plotted as a function of the atomic number *Z*.

The relativistic corrections made to EAs are found to work in the same manner as those for IPs. The *LS*-non-splitting correction is dominant for group 1 and groups 3–11 atoms, whereas the fine-structure correction is dominant for atoms of groups 13–17.

We first discuss group 1 and groups 3–11 atoms where the *LS*-non-splitting correction dominates. For all the first transition atoms except Cr and Cu and for the Zr and Tc atoms in the second transition series, the attached electron enters into the 3*d* or 4*d* orbital. This directly induces a large reorganization (expansion) of the outer 4*s* or 5*s* orbital and indirectly that of the inner *s* orbitals. Then $|E_{\mathrm{LS}}|$ in the anions is much smaller than in the neutrals, and EA_{LS} gives a marked negative contribution. For the remaining atoms in this category (except Y), the electron enters into the outermost *s* orbital and the electron attachment slightly expands the electron density distribution. This reduces $|E_{\mathrm{LS}}|$ of an anion but the decrease is almost compensated by an increase of

Table 3. Comparison of the non-relativistic HF, relativistic HF, and experimental EAs (in eV)

Atom		Non-relativistic HF EA	Mass correction		Relativistic correction			Relativistic HF EA	Experimental EA
			Normal	Specific	LS-non-splitting	Fine-structure	Sum		
1	H	−0.32845	0.00018	0.00000	−0.00016	0.00000	−0.00016	−0.32843	0.754195
3	Li	−0.12231	0.00001	0.00000	−0.00002	0.00000	−0.00002	−0.12232	0.618
5	B	−0.26774	0.00001	0.00018	−0.00148	−0.00089	−0.00237	−0.26992	0.277
6	C	0.55034	−0.00003	0.00026	−0.00345	−0.00436	−0.00781	0.54277	1.2629
7	N	−2.14903	0.00008	0.00020	−0.00470	0.00482	0.00012	−2.14862	
8	O	−0.53477	0.00002	0.00026	−0.00819	−0.00362	−0.01181	−0.54631	1.4611103
9	F	1.36342	−0.00004	0.00030	−0.01319	−0.01838	−0.03157	1.33210	3.401190
11	Na	−0.10301	0.00000	0.00000	−0.00010	0.00000	−0.00010	−0.10310	0.547926
13	Al	0.04240	−0.00000	0.00004	−0.00538	−0.00328	−0.00866	0.03378	0.441
14	Si	0.96050	−0.00002	0.00007	−0.00922	−0.01681	−0.02603	0.93452	1.385
15	P	−0.54171	0.00001	0.00006	−0.01087	0.01174	0.00087	−0.54077	0.7465
16	S	0.91252	−0.00002	0.00008	−0.01473	−0.00430	−0.01903	0.89355	2.077104
17	Cl	2.58108	−0.00004	0.00010	−0.01917	−0.03518	−0.05435	2.52680	3.61269
19	K	−0.07809	0.00000	0.00000	−0.00008	0.00000	−0.00008	−0.07817	0.50147
22	Ti	−0.91015	0.00001	0.00024	−0.14738	−0.00836	−0.15574	−1.06563	0.079
23	V	−0.57703	0.00001	0.00026	−0.17864	−0.01671	−0.19535	−0.77212	0.525
24	Cr	−0.52461	0.00003	0.00000	−0.01820	0.00000	−0.01820	−0.54279	0.666
25	Mn	−3.73183	0.00003	0.00027	−0.21385	0.04152	−0.17233	−3.90386	
26	Fe	−2.08415	0.00000	0.00027	−0.25766	0.01690	−0.24077	−2.32464	0.151
27	Co	−1.70732	0.00003	0.00030	−0.29913	−0.01747	−0.31660	−2.02360	0.662
28	Ni	−1.35445	0.00000	0.00030	−0.34444	−0.05489	−0.39933	−1.75348	1.156
29	Cu	0.01097	−0.00000	0.00000	0.01967	0.00000	0.01967	0.03064	1.235
31	Ga	−0.01712	0.00000	0.00003	−0.03206	−0.02340	−0.05546	−0.07255	0.3
32	Ge	0.95262	−0.00000	0.00003	−0.04397	−0.10003	−0.14400	0.80864	1.233
33	As	−0.42760	0.00000	0.00003	−0.04912	0.05916	0.01004	−0.41753	0.81
34	Se	1.00992	−0.00000	0.00005	−0.05372	−0.01739	−0.07110	0.93887	2.020670
35	Br	2.58345	−0.00000	0.00003	−0.05829	−0.13834	−0.19663	2.38685	3.363590
37	Rb	−0.06950	0.00003	0.00000	0.00003	0.00000	0.00003	−0.06944	0.48592
39	Y	−0.02868	0.00000	0.00000	−0.01899	−0.04128	−0.06027	−0.08895	0.307
40	Zr	−0.01537	0.00000	0.00008	−0.38934	−0.01690	−0.40624	−0.42153	0.426
41	Nb	−0.53095	0.00000	0.00000	−0.03238	0.00629	−0.02610	−0.55704	0.893
42	Mo	−0.63218	0.00000	0.00000	−0.05671	0.00000	−0.05671	−0.68888	0.746
43	Tc	−0.65596	0.00000	0.00011	−0.56687	0.09519	−0.47168	−1.12753	0.55
44	Ru	−0.29962	0.00000	0.00000	−0.00601	−0.00003	−0.00604	−0.30567	1.05
45	Rh	−0.16659	0.00000	0.00000	0.01701	−0.00035	0.01665	−0.14993	1.137
47	Ag	0.04291	−0.00000	0.00000	0.05967	0.00000	0.05967	0.10259	1.302
49	In	0.16286	−0.00000	0.00003	−0.07891	−0.05358	−0.13249	0.03040	0.3
50	Sn	1.11463	−0.00000	0.00003	−0.09127	−0.23053	−0.32180	0.79286	1.112
51	Sb	−0.10348	0.00000	0.00003	−0.09829	0.12874	0.03045	−0.07301	1.07
52	Te	1.19431	−0.00000	0.00003	−0.09780	−0.03325	−0.13105	1.06329	1.9708
53	I	2.58473	−0.00000	0.00003	−0.09728	−0.26732	−0.36461	2.22015	3.059038

$|E_{\mathrm{LS}}|$ by the contribution of the added electron. As a consequence, $|EA_{\mathrm{LS}}|$ is expected not to be large for these atoms. We find a similar conclusion for the Y atom where a *p* electron attaches. In fact, Table 3 and Fig. 2 show that $|EA_{\mathrm{LS}}|$ of the *s* or *p* electron attachment is much smaller than that of the *d* electron attachment.

For the atoms of groups 13–17, the attached electron enters into the outermost *p* orbital, and the *LS*-non-splitting correction remains almost unchanged between an anion and its parent neutral atom. Thus the fine-structure correction is important for EAs, as it has been for IPs, of these atoms. Negative EA_{FS} contributions found for group 14 (C, Si, Ge, Sn) and group 17 (F, Cl, Br, I) atoms can be understood by the fact that the ground state of their anions is either $p(3)$, ^{4}S or $p(6)$, ^{1}S and $E_{\mathrm{FS}}(\text{anion}) = 0$ in Eq. (11). Similarly, positive EA_{FS} in group 15 atoms (N, P, As, Sb) is explained by the fact that $E_{\mathrm{FS}}(\text{neutral}) = 0$ and only $-E_{\mathrm{FS}}(\text{anion})$ contributes in Eq. (11).

3.3 Correlation corrections

The last columns of Tables 2 and 3 give the experimental values [24] of IPs and EAs, respectively. For the hydrogen atom, the present relativistic HF IP agrees with the experimental value completely. For the other atoms, however, there are non-negligible discrepancies between the relativistic HF and experimental values both in the IPs and EAs. The differences are due to the electron correlation correction according to Eq. (1). In other words, the comparison of the present and experimental IPs in Table 2 and EAs in Table 3 predicts the magnitude of the correlation correction. In Table 4, we summarize the estimated correlation corrections for IPs and EAs for some atoms and compare them with the corresponding values directly obtained from correlated calculations [37–41]. We find a good agreement, though the number of atoms for which accurate non-relativistic correlated energies are known is limited. The remaining

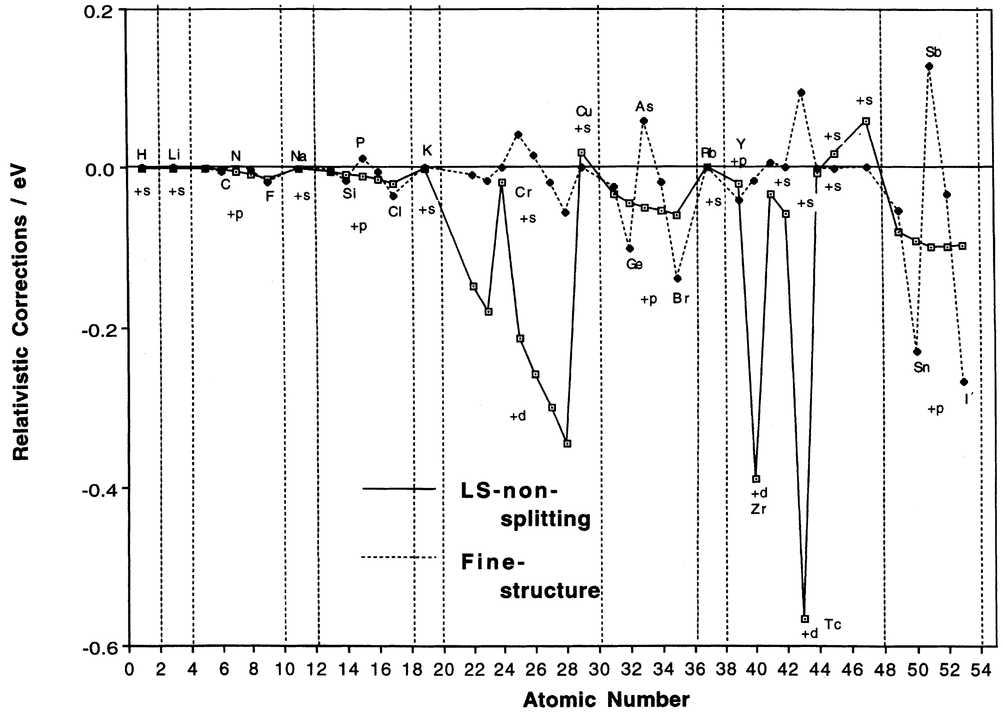


Fig. 2. *LS*-non-splitting and fine-structure contributions to electron affinities (EAs) as a function of atomic number *Z*

Table 4. Comparison of estimated and calculated electron correlation corrections (in eV) for some atoms

Atom	Estimated	Calculated
Ionization potential		
He	1.14411	1.14393
Li	0.04991	0.04993
Be	1.27768	1.27810
Electron affinity		
H	1.08262	1.08300
B	0.54692	0.541
C	0.72013	0.714
O	2.00742	1.989
F	2.06909	2.000

[a] Non-relativistic correlated energies were taken from [37] for H^-, He, Li^+, from [38] for Li, from [39] for Be^+, and from [40] for Be. Non-relativistic correlated EAs were taken from [41] for B,C,O, and F

atoms await the results of accurate correlation calculations for comparison. Nonetheless, the agreement shown in Table 4 suggests that the present data in Tables 2 and 3 could be used as a reference for such calculations.

4 Summary

Within the HF approximation, the relativistic and mass corrections to IPs and EAs have been studied for the atoms with $Z \leq 54$. The mass correction is not important except for IPs of very light atoms. Of the two components of the relativistic correction, the *LS*-non-splitting correction has been found to give a significant contribution to IPs and EAs of atoms of groups 3–12 or transition atoms. On the other hand, the fine-structure correction is more important than the *LS*-non-splitting correction for IPs and EAs of atoms of groups 13–18. The different contribution of these two corrections can be explained by the character of the orbital which an electron is removed from or added to. The comparison of the present results with experimental values gives an estimation of the electron correlation correction to IPs and EAs. For some light atoms for which correlated total energies are accurately known, the estimated correlation corrections have been confirmed to agree with the calculated values. The present numerical results suggest that in order to discuss IPs and EAs, as well as excitation energies, within the accuracy of 1 eV, one can confidently include the relativistic corrections for the atoms with $Z \geq 21$.

Acknowledgements. This work was supported in part by a Grant-in-Aid for Scientific Research form the Ministry of Education, Japan and in part by Grant (PB94-0160) from DGICYT, Spain.

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